

PATENT SPECIFICATION

(11)

1 394 146

- (21) Application No. 38923/73 (22) Filed 17 Aug. 1973
 (31) Convention Application No. 2 241 015 (32) Filed 21 Aug. 1972 in (19)
 (33) Germany (DT)
 (44) Complete Specification published 14 May 1975
 (51) INT CL² C09B 51/00; D06P 1/32, 3/08
 (52) Index at acceptance
 C4P DIN
 D1B 2A4 2S

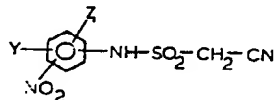


(54) α -CYANOMETHANE-SULPHONAMIDO-NITRO-
 BENZENE DERIVATIVES AND THEIR USE AS HAIR DYES

(71) We, HENKEL & CIE. GMBH a German Company, of 67, Henkelstrasse Duesseldorf-Holthausen 4000, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to α -cyanomethane-sulphonamido-benzene derivatives.

The invention provides compounds of the formula:



in which Y represents hydrogen, chlorine, bromine, or an alkoxy group having 1—4 carbon atoms, and Z represents NH_2 — or OH group.

Examples of compounds of the described type are:

- 2 - amino - 3 - (α -cyanomethane - sulphonamido) - 1 - nitro - benzene,
 2 - amino - 4 - (α -cyanomethane - sulphonamido) - 1 - nitro - benzene,
 1 - amino - 4 - (α -cyanomethane - sulphonamido) - 2 - nitro - benzene,
 2 - amino - 4 - chloro - 1 - (α -cyanomethane - sulphonamido) - 3 - nitro - benzene,
 1 - amino - 5 - (α -cyanomethane - sulphonamido) - 4 - methoxy - 2 - nitro - benzene,
 2 - amino - 3 - chloro - 4 - (α -cyanomethane - sulphonamido) - 1 - nitro - benzene,
 1 - amino - 3 - (α -cyanomethane - sulphonamido) - 2 - nitro - benzene,
 1 - amino - 2 - (α -cyanomethane - sulphonamido) - 4 - nitro - benzene,
 2 - amino - 1 - (α -cyanomethane - sulphonamido) - 4 - nitro - benzene,
 1 - amino - 5 - bromo - 2 - (α -cyanomethane - sulphonamido) - 4 - nitro - benzene,
 1 - amino - 2 - (α -cyanomethane - sul-

- phonamido) - 3 - nitro - benzene,
 1 - amino - 3 - (α -cyanomethane - sulphonamido) - 5 - nitro - benzene,
 1 - amino - 2 - chloro - 3 - (α -cyanomethane - sulphonamido) - 5 - nitro - benzene,
 1 - amino - 2 - butoxy - 4 - (α -cyanomethane - sulphonamido) - 5 - nitro - benzene,
 4 - amino - 2 - (α -cyanomethane - sulphonamido) - 1 - nitro - benzene,
 2 - amino - 1 - ethoxy - 4 - (α -cyanomethane - sulphonamido) - 5 - nitro - benzene,
 2 - (α -cyanomethane - sulphonamido) - 4 - nitro - phenol,
 2 - (α -cyanomethane - sulphonamido) - 6 - nitro - phenol,
 4 - chloro - 2 - (α -cyanomethane - sulphonamido) - 6 - nitro - phenol,
 2 - (α -cyanomethane - sulphonamido) - 3 - methoxyl - 6 - nitro - phenol,
 6 - chloro - 2 - (α -cyanomethane - sulphonamido) - 4 - nitro - phenol,
 2 - (α -cyanomethane - sulphonamido) - 5 - nitro - phenol,
 4 - bromo - 5 - (α -cyanomethane - sulphonamido) - 2 - nitro - phenol,
 4 - (α -cyanomethane - sulphonamido) - 2 - nitro - phenol,
 3 - (α -cyanomethane - sulphonamido) - 2 - nitro - phenol,
 2 - (α -cyanomethane - sulphonamido) - 5 - nitro - phenol,
 2 - (α -cyanomethane - sulphonamido) - 3 - methoxy - 5 - nitro - phenol,
 5 - chloro - 2 - (α -cyanomethane - sulphonamido) - 4 - nitro - phenol,
 2 - (α -cyanomethane - sulphonamido) - 3 - nitro - phenol,
 5 - butoxy - 2 - (α -cyanomethane - sulphonamido) - 3 - nitro - phenol,
 3 - (α -cyanomethane - sulphonamido) - 5 - nitro - phenol,
 2 - bromo - 4 - (α -cyanomethane - sulphonamido) - 3 - nitro - phenol,
 2 - ethoxy - 5 - (α -cyanomethane - sulphonamido) - 4 - nitro - phenol.

The compounds in accordance with the

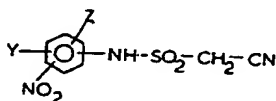
[Price 33p]

invention may be produced by reacting the corresponding nitro-amino-phenols or diamino-nitro-benzenes, substituted if required, with the stoichiometric quantity of chlorosulphonyl-acetonitrile required for the monosubstitution of an amino group. Advantageously, reaction is effected in the presence of a solvent such as hydrocarbons, benzene, chlorobenzene, tetrahydrofuran, in such a manner that the chlorosulphonyl acetonitrile dissolved in the particular solvent is added to the nitro-amino phenols or diamino-nitrobenzenes drop by drop under ice cooling. After the said substances have been added, the reaction mixture is maintained for a few hours at room temperature under agitation and is subsequently poured into water and the reaction product, obtained in the form of an oil or in solid form, is separated. The reaction product can be purified by recrystallization from ethanol.

The compounds in accordance with the invention are valuable hair dyes. They may be used as direct dyes which produce yellows of various tints. Compared with the starting substances used for their production, which are known as direct soakers, they are characterised by better absorption and fastness properties, and also provide widely differing tints.

Furthermore, the compounds in accordance with the invention can be used as yellow couplers in oxidation dyes in combination with conventional developer substances, and the colour tints obtainable can be varied by means of the developer components, and the intensity of the oxidation can be varied through various tints of yellow to brown.

Consequently, a further object of the invention is the use of compounds of the general formula:



in which Y represents hydrogen, chlorine, bromine, or an alkoxy group having 1-4 carbon atoms, and Z represents an NH_2 - or OH - group in preparations for dyeing hair.

A particular embodiment of this subject of the invention relates to the use of compounds of the above-mentioned formulas in combination with conventional developer substances in preparations for the oxidative dyeing of hair.

In this instance, suitable developer substances are the compounds which are normally used for this purpose. The most important examples are primary aromatic amines having a further functional group in the *p*-position, such as *p*-phenylenediamine, *p*-toluylenediamine, *p*-dimethylaminoaniline, *p*-aminophenol, *p*-diaminoanisole or other compounds of the said kind which also con-

tain two or more functional groups in the form of

OH —, NH_2 —, NHR —, NR — (R = lower alkyl or hydroxyalkyl radical having 1-4 carbon atoms).

Further suitable developer substances are diaminopyridine derivatives, heterocyclic hydrazone derivatives and particularly 4-amino-pyrazolone derivatives in accordance with Austrian Patent Specification 277,465.

Advantageously, the coupler components in accordance with the invention are used in approximately molar quantities relative to the developer substances used. However, it is generally not disadvantageous if there is a certain excess or deficiency of colour coupler components.

The colour coupler components as well as the developer substances may be mixtures of compounds of the above-mentioned kind.

Basically, the oxidative coupling, i.e. the development of the colour, can be carried out by means of atmospheric oxygen in the same manner as in other oxidation dyes. Advantageously, however, chemical oxidation agents are used. Suitable chemical oxidation agents are particularly hydrogen peroxide or its products of addition to urea, melamine and sodium borate and mixtures of such products of addition of hydrogen peroxide with potassium peroxydisulphate.

When used in the manner described above, the compounds in accordance with the invention may be present in the form of aqueous solutions. Such solutions should contain the dyes or the combinations of dyes comprising coupler and developer components in quantities of from 0.2 to 5, particularly 2 percent by weight.

The compounds in accordance with the invention may also be used in the form of creams or emulsions. For this purpose, the dyes or mixtures of dyes may be mixed with the components normally present in such preparations. Such components include optional wetting or washing agents of the anionic or non-ionogenic type, such as alkylbenzene sulphonates, fatty alcohol sulphates, alkylsulphonates, fatty acid, ethanolamides, products of addition of ethylene oxide to fatty acids and fatty alcohols. Furthermore, such preparations may contain thickening agents such as methyl cellulose, starches and higher fatty alcohols, paraffin oil and fatty acids, and perfume oils or hair lotions such as pantothenic acid and cholesterol.

The additives are used in the quantities normally used for these purposes. Suitable quantities of wetting agent additives are particularly from 0.5 to 30% relative to the total composition, and suitable quantities of the thickening agent additives are from 0.1 to 25% relative to the total composition. According to the purpose for which they are used, the concentration of the dyes or of the combinations of dyes in such agents, present in the form

of creams or emulsions, is up to 5%, preferably 0.1 to 2% relative to the total composition.

5 Colouring can be carried out at temperatures of between 15 and 40° C in a weakly acid, neutral or preferably alkaline medium.

10 The colours obtained have satisfactory fastness properties with respect to light, washing and rubbing, and can readily be removed by means of reduction agents.

EXAMPLES.

Example 1.

15 1 - amino - 2 - (α - cyanomethane - sulphonamido) - 4 - nitro - benzene)

A solution of 14 g (0.1 mol) of chlorosulphonyl - acetonitrile in 50 ml of absolute tetrahydrofuran is slowly added drop by drop, with ice cooling, to a solution of 15.3 g (0.1 mol) of 1,2 - diamino - 4 - nitro - benzene in 200 ml of absolute tetrahydrofuran. The resultant mixture is subsequently agitated for six hours at room temperature. The mixture is then filtered and the filtrate is poured into water, and an oil is precipitated which is separated from the aqueous phase. This oil solidifies to a crystal paste after a period of time. The paste is filtered off and re-crystallized three times from ethanol.

Melting point: 185—187° C.

30 Analysis calculated for $C_9H_8N_4O_3S$
calculated: C 37.50 H 3.12 N 21.88
found: C 37.72 H 2.86 N 22.07

Example 2.

35 4 - amino - 2 - (α - cyanomethane - sulphonamido) - 1 nitro - benzene.

15.3 g (0.1 mol) of 1,3 - diamino - 4 - nitro - benzene dissolved in 100 ml of absolute tetrahydrofuran, and 14 g (0.1 mol) of chlorosulphonyl - acetonitrile dissolved in 50 ml of absolute tetrahydrofuran are reacted in the manner described in Example 1. The precipitate is recrystallized twice from ethanol.

Melting point: 216—217° C.

45 Analysis calculated for $C_9H_8N_4O_3S$
calculated: C 37.50 H 3.12 N 21.88
found: C 37.47 H 2.82 N 22.32

Example 3.

50 1 - amino - 4 - (α - cyanomethane - sulphonamido) - 2 - nitro - benzene.

15.3 g (0.1 mol) of 1,4 - diamino - 2 - nitro - benzene dissolved in 200 ml of absolute tetrahydrofuran, and 14 g (0.1 mol) of chlorosulphonyl - acetonitrile dissolved in 50 ml of absolute tetrahydrofuran are reacted in the manner described in Example 1. The reaction product is recrystallized from ethanol, the precipitate filtered off is washed with a little ether and is subsequently recrystallized again from water.

Melting point: 157—162° C.

Analysis calculated for $C_9H_8N_4O_3S$
calculated: C 37.50 H 3.12 N 21.88
found: C 37.51 H 2.79 N 22.07

Example 4.

65 4 - chloro - 2 - (α - cyanomethane - sulphonamido) - 6 - nitro - phenol

18.8 g (0.1 mol) of 2 - amino - 4 - chloro - 6 - nitro - phenol suspended in 100 ml of absolute tetrahydrofuran, and 14.0 g (0.1 mol) of chlorosulphonyl - acetonitrile dissolved in 50 ml absolute tetrahydrofuran, are reacted in the same manner as described in Example 1. The precipitate is recrystallized twice from ethanol.

Melting point: 174—177° C

Analysis calculated for $C_9H_6N_4O_3SCl$
calculated: C 32.93 H 2.19 N 14.41
found: C 33.51 H 2.06 N 14.53

Example 5.

80 6 - chloro - 2 - (α - cyanomethane - sulphonamido) - 4 - nitro - phenol.

18.8 g (0.1 mol) 2 - amino - 6 - chloro - 4 - nitro - phenol suspended in 100 ml of absolute tetrahydrofuran, and 14.0 g (0.1 mol) of chlorosulphonyl - acetonitrile dissolved in 50 ml of absolute tetrahydrofuran, are reacted in the same manner as described in Example 1. The precipitate is recrystallized twice from ethanol.

Melting point: 182—184° C

Analysis calculated for $C_9H_6N_4O_3SCl$
calculated: C 32.93 H 2.19 S 10.94
found: C 33.08 H 1.72 S 10.60

Example 6.

95 2 - (α - cyanomethane - sulphonamido) - 4 - nitro - phenol.

15.4 g (0.1 mol) of 2 - amino - 4 - nitro - phenol dissolved in 100 ml of absolute tetrahydrofuran, and 14.0 g (0.1 mol) of chlorosulphonyl - acetonitrile dissolved in 50 ml of absolute tetrahydrofuran, are reacted in the same manner as described in Example 1. The reaction product is recrystallized twice from ethanol and once from water.

Melting point: 166—168° C

Analysis calculated for $C_9H_7N_4O_3S$
calculated: C 37.36 H 2.74 N 16.34
found: C 37.11 H 2.62 N 16.43

Example 7.

110 4 - (α - cyanomethane sulphonamido) - 2 - nitro - phenol.

15.4 g (1.0 mol) of 4 - amino - 2 - nitro - phenol dissolved in 100 ml of absolute tetrahydrofuran, and 14.0 g (0.1 mol) of chlorosulphonyl - acetonitrile dissolved in 50 ml of absolute tetrahydrofuran, are reacted in the same manner as described in Example 1. The precipitate is recrystallized from ethanol.

Melting point: 150—155° C
 Analysis calculated for $C_{11}H_{10}N_2O_5S$
 calculated: C 37.36 H 2.74 N 16.34
 found: C 37.71 H 2.74 N 16.29

- 5 Example 8.
 2 parts by weight of 1 - amino - 2 - (α -cyanomethane sulphonamido) - 4 - nitro-benzene were incorporated in a cream base of the composition:

- 10 10 parts by weight of fatty alcohols $C_{12}-C_{18}$
 10 parts by weight of fatty alcohol sulphate (commercial mixture $C_{12}-C_{18}$)
 75 parts by weight of water

and the pH value of the mixture was adjusted to 9.5 by adding ammonia. This emulsion was made up to 100 parts by weight with water. The dyeing cream thus obtained was applied to human hair which had turned grey naturally, and was allowed to act for thirty minutes at room temperature. The hair was subsequently washed and dried. The result was hair which had been dyed a deep yellow colour.

Examples 9 -14.
 Using the same procedure as stated in Example 8, but with the use of the dye components in Examples 2 to 7, listed in the following table, the hair colours given were obtained.

Example No.	Dye component	Hair colour obtained
9	4-amino-2-(α -cyanomethane-sulphonamido)-1-nitro-benzene	olive-yellow
10	1-amino-4-(α -cyanomethane-sulphonamido)-2-nitro-benzene	topaz-yellow
11	4-chloro-2-(α -cyanomethane-sulphonamido)-6-nitro-phenol	pompeian yellow
12	6-chloro-2-(α -cyanomethane-sulphonamido)-4-nitro-phenol	honey yellow
13	2-(α -cyanomethane-sulphonamido)-4-nitro-phenol	olive-green
14	4-(α -cyanomethane-sulphonamido)-2-nitro-phenol	ivory

- Example 15.
 Equimolar quantities of 4 - amino - 1-phenyl - 3 - carbamoyl - pyrazolone - 5 acting as a developer component, and 1 - amino - 2-(α - cyanomethane - sulphonamido) - 4-nitro - benzene acting as a coupler component, were emulsified in a cream base as described in Example 8. The molar concentrations are so calculated that, assuming 100% reaction, 2 g dye are present in 100 g cream (corresponding to a 2% concentration of dye) upon the subsequent oxidative coupling reaction. The emulsion is adjusted to a pH value of 9.5 by adding ammonia and is subsequently made up to 100 parts by weight with water. The dyeing cream thus obtained dyed human hair yellowish brown with 30 minutes by virtue of the action of the atmospheric oxygen or a 1% or 9% solution of hydrogen peroxide, various tints of colour being obtained in accordance with the oxidation agents use (or their different concentrations).

- 55 Examples 16 to 52.
 Following the same procedure as in Example

15, but with the use of the developers and couplers given in the following Table as dye components a) and b), human hair which had turned grey naturally was dyed and the colours given in the last column were obtained (with atmospheric oxygen and a 1% and a 9% H_2O_2 solution). The dye components were used in equimolar quantities. The total quantity of the dye to be formed was 2 g in 100 g of the cream base in each case, and the reaction time was 30 minutes at room temperature.

The developer components under a) are abbreviated in the Table as follows:

- 4 - amino - 1 - phenyl - 3 - pyrazolone = A 70
 4 - amino - 1 - phenyl - 3 - ethoxycarbonyl-pyrazolone - 5 = B
 4 - amino - 1H - 3 - ethoxycarbonyl-pyrazolone - 5 = C
 p - toluylene - diamine = D 75
 1 - methyl - pyridone - 2 - hydrazone = E
 1 - methyl - quinoline - 4 - hydrazone = F

Example No.	Dye components a) developer b) coupler	Tint of the dyed hair by air oxidation	1% H ₂ O ₂ solution	9% H ₂ O ₂ solution
16	B 1-amino-2-(α -cyanomethane-sulpho-amido)-4-nitro-benzene	olive-brown	brass yellow	reddish yellow
17	C ditto	linoleum brown	olive-brown	toffee brown
18	D ditto	olive-brown	nut brown	hazel-nut brown
19	E ditto	olive	olive	—
20	F ditto	yellowish brown	yellowish brown	light brown x)
21	A 4-amino-2-(α -cyanomethane-sulphonamido)-1-nitro-benzene	olive brown	olive	olive
22	B ditto	olive brown	honey yellow	honey blonde
23	C ditto	olive brown	olive-yellow	olive-yellow
24	D ditto	olive brown	dark brown	linoleum brown
25	E ditto	olive yellow	olive-green	olive-brown x)
26	F ditto	olive yellow	olive-brown	golden yellow x)
27	A 1-amino-4-(α -cyanomethane-sulphonamido)-2-nitro-benzene	sooty brown	cocoa brown	Titian red
28	B ditto	cinnamon brown	light brown	autumn gold
29	C ditto	brown	cinnamon brown	autumn gold
30	D ditto	autumn gold	dark brown	reddish brown

x) with 4% H₂O₂ solution.

Example No.	Dye components a) developer	b) coupler	Tint of the dyed hair by air oxidation	1% H ₂ O ₂ solution	9% H ₂ O ₂ solution
31	E	1-amino-4-(α -cyanomethane-sulphonamido)-2-nitro-benzene	cognac brown	dark brown	dark brown x)
32	F	ditto	terra di Siena	hazel-nut brown	dark brown x)
33	A	2-(α -cyanomethane-sulphonamido)-4-chloro-6-nitro-phenol	somali brown	roe brown	Titian red
34	B	ditto	brick red	terra di Siena	brownish orange
35	C	ditto	Titian red	autumn gold	reddish gold
36	D	ditto	brick red	beaver brown	umber
37	E	ditto	brick red	somali brown	dark brown x)
38	F	ditto	reddish gold	reddish gold	autumn gold x)
39	A	2-(α -cyanomethane-sulphonamido)-5-chloro-4-nitro-phenol	bronze-brown	bronze-brown	yellowish brown
40	B	ditto	olive-brown	olive-brown	dark yellow
41	C	ditto	yellowish brown	olive-brown	dark yellow
42	D	ditto	olive-brown	sooty-brown	yellowish brown
43	E	ditto	dark yellow	yellow	-
44	A	2-(α -cyanomethane-sulphonamido)-4-nitro-phenol	olive-brown	brown	bronze-brown
45	B	ditto	khaki	khaki	greyish yellow

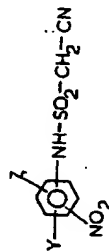
x) with 4% H₂O₂ solution

Example No.	Dye components a) Developer	b) coupler	Tint of the dyed hair by air oxidation	1% H ₂ O ₂ solution	9% H ₂ O ₂ solution
46	C	2-(α -cyanomethane-sulphonamido)-4-nitro-phenol	clay coloured	honey yellow	honey yellow
47	D	ditto	golden yellow	sooty brown	linoleum brown
48	F	ditto	ochre yellow	auburn	—
49	A	4-(α -cyanomethane-sulphonamido)-2-nitro-phenol	greyish brown	greyish brown	reddish grey
50	D	ditto	nougat brown	nutria brown	beaver brown
51	E	ditto	olive-brown	violet-brown	violet-brown x)
52	F	ditto	Pompeian yellow	brown	brown x)

x) with 4% H₂O₂ solution.

WHAT WE CLAIM IS:—

1. A compound of the formula:



5 in which Y represents hydrogen, chlorine, bromine or an alkoxy group having 1 to 4 carbon atoms, and Z represents an NH₂ or OH group.

10 2. A composition for dyeing hair which contains at least one compound as claimed in claim 1.

3. A composition for the oxidative dyeing of hair which comprises a compound as claimed in claim 1 and a colour developer substance.

4. A composition as claimed in claim 2 or claim 3 which is in the form of an emulsion or cream.

5. A compound as claimed in claim 1 and substantially as hereinbefore described with reference to any one of Examples 1 to 7.

6. A composition as claimed in claim 2 and substantially as hereinbefore described with reference to any one of Examples 8 to 14.

7. A composition as claimed in claim 3 and substantially as hereinbefore described with reference to any one of Examples 15 to 52.

W. P. THOMPSON & CO.,
Coopers Buildings,
12 Church Street,
Liverpool L1 3AB,
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.